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Communication

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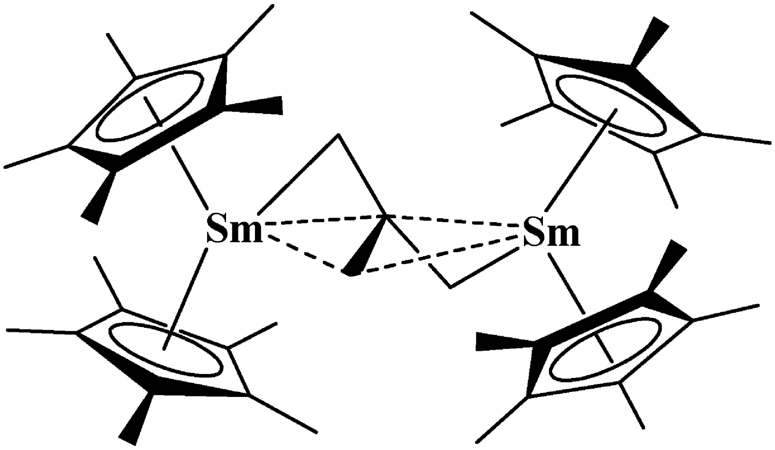

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Formation of a Bridging Planar Trimethylenemethane Dianion from a Neopentyl Precursor via Sequential β-Alkyl Elimination and C−H Activation

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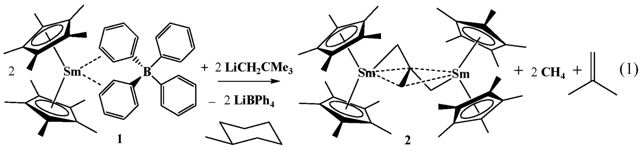
In 1982, an investigation of propene oligomerization by $[(C_5Me_5)_2LuMe]_2$ revealed the first example of β-alkyl elimination in metallocene chemistry.[1,2] Prior to the Lu report, the most closely related example in the literature involved the decomposition of $(Me_3CCH_2)_3Al$ to trimethylaluminum and isobutene.[3] Although β-alkyl elimination has subsequently been observed with a variety of transition metals[4−23] and is viewed as relatively facile in Sc metallocene chemistry,[7,8] the only example of lanthanide-based β-alkyl elimination in the literature since the initial report over 20 years ago[1,2] involves a 1996 study on β-alkyl shifts in the ring-opening polymerization of strained, small-ring methylenecycloalkanes.[24] Since β-alkyl elimination is much less common than β-hydrogen elimination, fewer examples are expected, and experimental examples are still considered to be in short supply.[20]

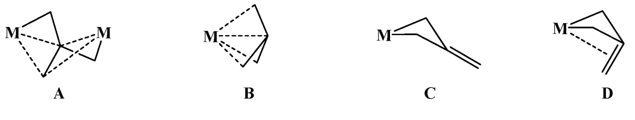
The paucity of data on β-alkyl elimination with lanthanides may arise from the experimental difficulties in accessing the requisite complexes for study, e.g., synthetic access to $[(C_5Me_5)_2LuMe]_2$ originally required a multistep preparation of five highly air-sensitive intermediates.[2] Recently, we have developed a facile synthetic route to unsolvated lanthanide alkylmetallocenes, $[(C_5Me_5)_2LnR]_x$,[25] that are now readily available by displacement of the loosely ligated $[BPh_4]^{1-}$ ion in $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$[26] using RLi reagents. We report here that this reaction with neopentyllithium provides a new approach to lanthanide-based β-alkyl elimination.

Reaction of Me_3CCH_2Li[27] with $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$, **1**, in methylcyclohexane in silylated glassware does not lead to the isolation of the expected $[(C_5Me_5)_2Sm(CH_2CMe_3)]_x$ but instead generates the trimethylenemethane dianion complex $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}C(CH_2)_3]$, **2**, eq 1.[28]



The NMR spectra of **2** were not structurally definitive due to paramagnetism, but the ^{13}C NMR spectrum contained C_5Me_5 ring and methyl resonances at δ 116.2 and 17.5 ppm, respectively, consistent with the presence of Sm(III) not Sm(II).[29] **2** was identified by X-ray crystallography[30] (Figure 1) and independent synthesis as described below.

The trimethylenemethane (TMM) ligand in **2** (A) is unusual in several ways compared to previously reported TMM complexes (B−D).[31−37] To our knowledge, it is the first bridging TMM ligand to be reported. It is also unusual in that the four carbon atoms are planar to within 0.01 Å. This matches calculations for the free TMM dianion.[38−40] The orbital advantages of puckering TMM ligands upon complexation to a metal were delineated long ago,[32] and structural studies typically show that the θ-angle that defines the pyramidal arrangement of the central carbon and the three methylene carbons is approximately 12°. The four X-ray crystal structures[33,34,36] of early transition metal TMM complexes most closely related to **2** have nonplanar B−D-type structures.



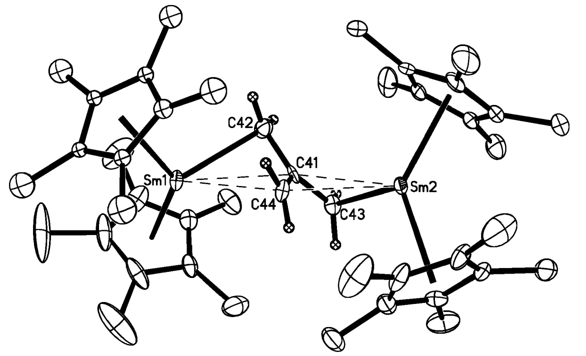


Figure 1. Thermal ellipsoid plot of $[(C_5Me_5)_2Sm]_2[\mu\text{-}\eta^3{:}\eta^3\text{-}C(CH_2)_3]$, **2**, with ellipsoids drawn at the 50% probability level. All hydrogen atoms depicted were located and refined isotropically. The nonbonding Sm1⋯C43 and Sm2⋯C42 distances are approximately 3.92 Å.

Although the C(central)−C(methylene) distances in **2**, 1.424(6) Å C(41)−C(44), 1.432(6) Å C(41)−C(42), and 1.426(6) Å C(41)−C(43), are indistinguishable, i.e., this six-electron ligand has a delocalized structure, the Sm−C distances consist of two types. The 2.546(4) Å Sm(1)−C(42) and 2.567(4) Å Sm(2)−C(43) lengths are somewhat longer than the range of typical Sm−C single bonds[41] and considerably shorter than the 2.734(4)−2.799(4) Å Sm−C(41, 44) distances. The range of Sm−C(TMM) distances in **2** is similar to the 2.551(17)−2.730(17) Å range of Sm−C(allyl) connections observed in the substituted allyl complexes $(C_5Me_5)_2Sm(CH_2CHCHR)$ (R = Me, $CH_2CH_2CHCHCH_2$).[42] The fact that the TMM ligand in **2** resembles an allyl group bound on each side to a metal may account for its planarity.[43]

One route by which **2** could be formed from "$[(C_5Me_5)_2Sm(CH_2CMe_3)]_x$", the likely initial product of the $Me_3CCH_2Li/[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$ reaction, involves β-methyl elimination to make $[(C_5Me_5)_2SmMe]_3$, **3**, and isobutene, $CH_2{=}CMe_2$, as shown in eq 2. Subsequent C−H activation of the isobutene by **3** could generate a 2-methylallyl complex, $(C_5Me_5)_2Sm[CH_2C(Me)CH_2]$, **4**, eq 3, which could be metalated again by **3** to form **2**, eq 4.

The overall transformation of a neopentyl group to a TMM ligand has been observed using Ru in the reaction of 2 equiv of Me_3CCH_2MgCl with $[MeSi(CH_2PMe_2)_3](PMe_3)RuCl_2$.[12] In the Ru case, two cyclometalation/elimination reactions are coupled with a β-methyl elimination from a $\overline{RuCH_2C(Me)_2CH_2}$ metallacycle. The fact that this type of transformation can be done with an f element was unexpected since TMM complexes of these metals were

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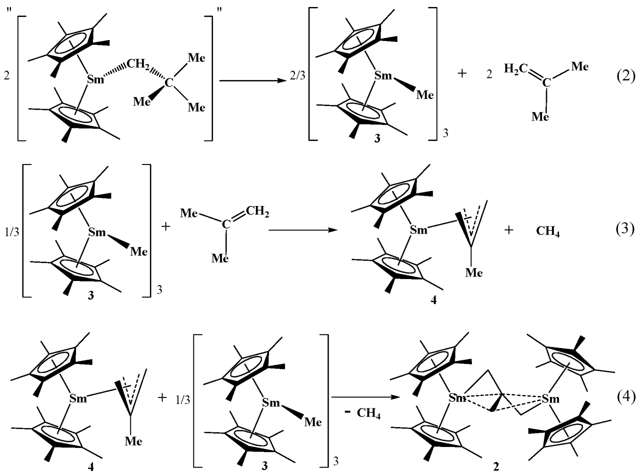

previously unknown. The reaction becomes possible since $[(C_5Me_5)_2SmMe]_3$ is such a powerful metalation reagent (e.g., it metalates Me_4Si to $[(C_5Me_5)_2Sm(CH_2SiMe_3)]_x$).[25] Interestingly, $(C_5Me_5)_2Sc(CH_2CMe_3)$ is not observed to undergo β-methyl elimination.[44] Since Sm is larger than Sc, the Sm complex is less sterically saturated and hence more reactive.[45]

The following data are consistent with the steps in eqs 2−4. The reaction of Me_3CCH_2Li with **1** under hydrogen forms CMe_4 in C_6D_{12}, which is consistent with hydrogenolysis of $[(C_5Me_5)_2Sm(CH_2CMe_3)]_x$. Analysis of the gases generated in the Me_3CCH_2Li/**1** reaction shows methane and isobutene, which is consistent with eq 1. Consistent with eqs 3 and 4, 2 equiv of the independently isolated trimer, $[(C_5Me_5)_2SmMe]_3$, **3**, react with 3 equiv of isobutene, $CH_2{=}CMe_2$, to form CH_4 and **2**. When excess isobutene is reacted with **3**, CH_4 and the 2-methylallyl complex $(C_5Me_5)_2Sm[CH_2C(Me)CH_2]$, **4**, are formed. This is consistent with complete consumption of **3** by isobutene via eq 3 to make **4** before **3** can metalate **4** to make **2** via eq 4. Direct reaction of **3** with **4**, independently isolated from reactions of **3** or $[(C_5Me_5)_2Sm(CH_2SiMe_3)]_x$[25] and excess isobutene,[46] shows complete conversion of **4** to **2** with concomitant formation of CH_4 according to eq 4.

Deuterium labeling studies were also consistent with reactions proposed in eqs 2−4 but suggested an additional C−H activation pathway. Reaction of $[(C_5Me_5)_2SmMe]_3$ with excess isobutene-d_8 in cyclohexane-d_{12} gave $(C_5Me_5)_2Sm[CD_2C(CD_3)CD_2]$, **4-$d_7$**,[28] and the CH_3D[28] expected via eq 3, but CH_4 was also observed (CH_3D:CH_4 = 2). The CH_4 is consistent with $[(C_5Me_5)_2SmMe]_3$ metalation of ring methyl groups to form either $(C_5Me_4CH_2)^{2-}$ or $[(C_5Me_3(CH_2)_2]^{3-}$ ligands as has been previously observed for this complex[25] and found in other highly metalating systems.[46,47] The Sm−CH_2 linkages associated with these metalated rings can subsequently metalate the isobutene-d_8 to make the observed **4-d_7** and some DCH_2 pentamethylcyclopentadienyl units. Consistent with this scenario, the ^2H NMR spectrum of the **3**/isobutene-d_8 reaction products showed incorporation of deuterium into ring positions. Reaction of trimeric $[(C_5Me_5)_2SmMe]_3$ with 3 equiv of **4-d_7** in C_6H_{12} generated a resonance at δ 9.08 in the ^2H NMR, consistent with formation of **2-d_6**.[28] Again, deuterium incorporation into the ring methyl positions is also observed.

In summary, the $[(C_5Me_5)_2Sm][(\mu\text{-}Ph)_2BPh_2]$/RLi reaction not only provides alkyl complexes high in C−H activation reactivity like $[(C_5Me_5)_2SmMe]_3$,[25] but with R = neopentyl, it also provides new opportunities to study β-methyl elimination. In this case, the β-methyl elimination is followed by two C−H activation reactions that combine to generate a cascade of reactions that convert the neopentyl precursor to a trimethylenemethane dianion. The resulting **2** not only is the first f element TMM complex but it also reveals a new mode of binding for TMM as a planar bridging ligand.

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Supporting Information Available: Synthetic, spectroscopic, and X-ray diffraction details (PDF, CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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